

CD221. LECTURE 2. LARGER GAS SYSTEMS. THE EINSTEIN SOLID.

Our study of the 4-particle gas allowed us to draw a few preliminary conclusions. It allowed us to identify the condition of equilibrium as a state of a system in which a small number of macroscopic properties remain time-independent, barring small deviations from an average value. It also showed us that a system in constrained equilibrium tended to evolve to a condition of greater uniformity when the constraint was released.

How would these conclusions change – if at all – as N became bigger and bigger? Suppose N were, say, 100?

In this case, the number of microstates would be 2^{100} (because each of the 100 particles can exist in two states, left or right), and the number of macrostates would be 101 (because n_L could be 0, or 1, or 2, or 3, all the way up to 100.) It should be fairly clear that for this system many of the macrostates will have a large number of microstates that give rise to them, i.e., many of the macrostates will have large multiplicities. These multiplicities can be calculated.

For instance,

$\Omega(n_L = 0) = 1$. This is because there's only 1 arrangement of the 100 particles in which *no* particle is on the left – all the particles must be on the right.

To calculate $\Omega(n_L = 1)$, we can imagine that the 100 particles are first held in a bin. We then have to pick one of them from the bin, place it in the left half of the gas container, and then place the 99 others in the right half. There are clearly 100 choices for the first particle we pick, and so $\Omega(n_L = 1) = 100$. (It follows that $\Omega(n_L = 99)$ also equals 100 because to form this macrostate, it's enough to pick *one* particle to place in the *right* half of the box – all the others must go into the left.)

To calculate $\Omega(n_L = 2)$, we pick any two particles from the bin and place them in the left half of the box, placing the other 98 in the right half. There are 100 ways to pick the first particle. Having picked one, there are now 99 left in the bin, and so there are 99 ways to pick the second particle. So in total there are 100×99 ways to pick any two particles to place in the left half of the box. But this number is an overcount, because it distinguishes between choices that differ only in the *order* in which a *given* pair of particles is chosen. In other words, a selection in which, say, particle 3 is picked first and then, say, particle 17, would be counted as distinct from one in which particle 17 is picked first and then particle 3. But it should not be since all that matters is that particles 3 and 17 are both located in the left half of the box. So the number 100×99 should be divided by 2. Thus,

$$\Omega(n_L = 2) = \Omega(n_L = 98) = \frac{100 \times 99}{2}$$

The calculation of $\Omega(n_L = 3)$ proceeds similarly. There are 100 ways to pick the first particle to go into the left half of the box, 99 ways for the second, and 98 ways for the third, for a grand total of $100 \times 99 \times 98$ ways to pick any 3. But again this is an overcount, and it must be divided by the number of different ways the *order* of picking the particles could be made. If in a particular selection, the chosen particles were numbered, say, 5, 1 and 23, they could have been picked in 6 different orders: 5,1,23 or 5, 23, 1, or 1, 5, 23 or 1, 23, 5 or 23, 1, 5 or 23, 5, 1 – a total of $3! = 6$ ways. And so,

$$\Omega(n_L = 3) = \Omega(n_L = 97) = \frac{100 \times 99 \times 98}{3 \times 2 \times 1}$$

Thus, if $n_L = m$, say, then

$$\begin{aligned} \Omega(n_L = m) &= \Omega(n_L = 100 - m) = \frac{100 \times 99 \times 98 \times \cdots \times (100 - (m - 1))}{m \times (m - 1) \times (m - 2) \times \cdots \times 3 \times 2 \times 1} \\ &= \frac{100 \times 99 \times 98 \times \cdots \times (100 - m + 1))}{m!} \\ &= \frac{100 \times 99 \times 98 \times \cdots \times (100 - m + 1))}{m!} \times \frac{(100 - m)!}{(100 - m)!} \\ &= \frac{100!}{(100 - m)! \times m!} \end{aligned}$$

The last expression is given the symbol $\binom{100}{m}$, and it represents the number of combinations of 100 things taken m at a time.

With these formulas in hand, we can estimate the likelihood of seeing some of the macrostates in the above $N = 100$ particle system if we were to take a series of snapshots of it over a fairly long period of time. (It helps to have a software package like Mathematica do the calculations for you.) For instance,

$$p(n_L = 0) = \frac{\Omega(n_L = 0)}{\Omega_{\text{total}}} = \frac{1}{2^{100}} \approx 7.89 \times 10^{-31}$$

$$p(n_L = 25) = \frac{\Omega(n_L = 25)}{\Omega_{\text{total}}} = \binom{100}{25} \frac{1}{2^{100}} = \frac{100!}{75! \times 25! \times 2^{100}} \approx 1.91 \times 10^{-7}$$

$$p(n_L = 50) = \frac{\Omega(n_L = 50)}{\Omega_{\text{total}}} = \binom{100}{50} \frac{1}{2^{100}} = \frac{100!}{50! \times 50! \times 2^{100}} \approx 0.080$$

$$p(n_L = 75) = p(n_L = 25) \approx 1.91 \times 10^{-7}$$

$$p(n_L = 100) = p(n_L = 0) \approx 7.89 \times 10^{-31}$$

The most striking observation we can make about these results is the following: each of the 101 macrostates of this system occurs with almost negligible probability in absolute terms, but notice how much larger the probabilities are of the macrostates in which the particles are more or less uniformly distributed between the two halves than those in which the particles are concentrated in the left or right halves. Indeed, at any instant of time, the system is about 30 orders of magnitude *less* likely to be seen in the state where there are *no* particles in the left half than in the state where each half is equally populated.

So again, if we were somehow to constrain these 100 particles to initially occupy just the left half of the box, what macrostates would they then be seen most often in once the constraint were removed? Clearly those macrostates where the molecules are more or less uniformly distributed between the two sides of the box.

The picture that is emerging is that when systems are allowed to change their state they seem to want to do so in a direction that leads to the greatest uniformity in the distribution of their constituent particles. But we still have to regard this conclusion as tentative because it is based on the fate of a just single property of the system, viz., the positions of its particles. That may be too simplistic because it ignores another property of the particles that may be important, viz., their energy, which the particle possess by virtue of their motion or their potential. Let's therefore now turn our attention to systems where the energy plays a role. For this purpose, we'll consider another simple system whose macroscopic and microscopic details we can uncover in more or less complete detail. This system is the **Einstein solid**.

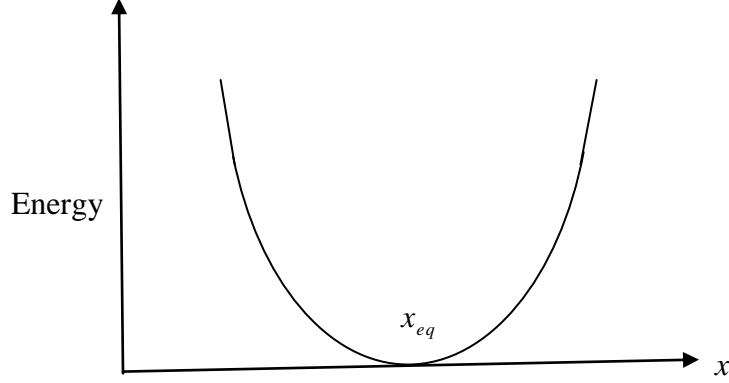
- The Einstein solid

This is a solid of N atoms on a lattice. Each atom is assumed to vibrate harmonically about its rest position, independent of what any of its neighbors is doing. (The atoms of a real solid are actually *strongly* coupled to each other, so this assumption is a bit of a stretch, but it is useful as a heuristic.) So each atom in this solid is an *independent, distinguishable* (because the lattice sites are distinguishable) harmonic oscillator.

As a function of its displacement x from its rest position x_{eq} , the energy E of an oscillator is, *in general*, given by the formula

$$E = \frac{1}{2}k(x - x_{eq})^2 \quad (1)$$

where k is the oscillator's spring constant. Graphically, the energy looks like this:



However, the continuous variation of E with x depicted in this figure is actually not consistent with what we know from quantum mechanics, which tells us that E is, in fact, limited to a set of *discrete* values E_n , which are given by the formula

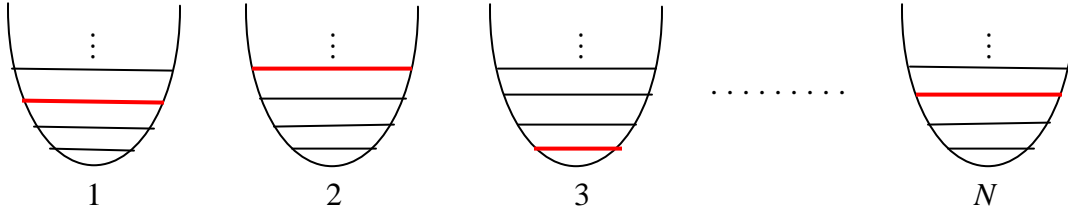
$$E_n = (n + 1/2)\hbar\omega, \quad n = 0, 1, 2, \dots, \infty \quad (2)$$

where $\hbar \equiv h/2\pi$, h being Planck's constant ($= 6.63 \times 10^{-34}$ J s), and $\omega \equiv \sqrt{k/m}$ is a frequency, with m the mass of the oscillator.

It's not too important to know where Eq. (2) comes from, but as Einstein showed, it *is* important to treat the oscillators of this N -atom model quantum mechanically, if the model is to bear any semblance to reality. So we'll assume that the energies of each atom in the solid are *quantized*, and that these energies are restricted to the following values:

$$\begin{aligned} E_0 &= \hbar\omega/2 \\ E_1 &= 3\hbar\omega/2 \\ E_2 &= 5\hbar\omega/2 \\ E_3 &= 7\hbar\omega/2 \\ &\vdots \\ E_l &= (l + 1/2)\hbar\omega \\ &\vdots \end{aligned} \quad (3)$$

But these values must be such that when they are all added up they equal the *thermodynamic* energy of the solid, which we can take to be U . So the macrostate of the solid is U, N , and its microstate is the set of energies that the N atoms have (which, as we've said, are constrained to sum to U .) A schematic illustration of one such microstate is shown below:



Here the black horizontal lines are the energy levels *available* to each oscillator and the red horizontal lines are the *actual* energy values the oscillators assume. We'll also assume that although these oscillators are all independent, they nevertheless manage to “communicate” with other in some way, and thereby make random transitions between the energy levels accessible to them. So in the same way that gas particles move back and forth between one side of a box and another, constantly change their state from left to right or right to left in the process, the particles of the Einstein solid have to be thought of as ceaselessly moving from one energy level to another.

It's a useful exercise to work out some of the properties of this model for specific values of N .

- The macro- and microstates of an $N = 3$ Einstein solid

To simplify matters a little, let's introduce oscillator energy states E'_n in which the “zero point energy” $\hbar\omega/2$ has been subtracted off, i.e.,

$$E'_n = E_n - \hbar\omega/2 = n\hbar\omega, \quad n = 0, 1, 2, \dots, \infty \quad (4)$$

This definition allows the energies to be represented as integers (in units of $\hbar\omega$.) We can now enumerate (in tabular form) some of the possible macrostates of this system and the microstates and multiplicities that are associated with them.

These quantities are shown in Table 1 below:

Table 1

Label	Macrostate (U)	Particle energy			Multiplicity Ω
		1	2	3	
1	0	0	0	0	1
2	1	1	0	0	3
3		0	1	0	
4		0	0	1	
5	2	2	0	0	6
6		0	2	0	
7		0	0	2	
8		1	1	0	
9		1	0	1	
10		0	1	1	
11	3	3	0	0	10
12		0	3	0	
13		0	0	3	
14		2	1	0	
15		2	0	1	
16		1	2	0	
17		0	2	1	
18		1	0	2	
19		0	1	2	
20		1	1	1	

What this table allows us to conclude is that if a “bulk” measurement of the energy U of a 3 atom Einstein solid established that it had, say, 3 units of energy, then microscopically it would have to exist – at some instant of time – in one of the 10 possible microstates listed above. Of course, it might exist in another microstate at some other instant of time because of our assumption that the oscillators can make random transitions between different energy levels, but this different microstate would still have to be one of the 10 that corresponds to a macrostate of energy 3.

In the above example, the calculation of the multiplicity is easily carried out by exhaustive enumeration of microstates. But what if the solid had N atoms and its bulk energy were U – is there a general formula for Ω in such a case?

- The multiplicity of an N -atom Einstein solid with U units of energy

The problem of calculating the multiplicity of an N -atom Einstein solid with U units of energy amounts to finding the number of ways that U units of energy can be divided amongst N oscillators. One way to think about the problem is to imagine that energy units are “balls” (each one represented as a dot \bullet) and oscillators are “bins” (each one represented as a tray $| _ _ |$). In this view, if U were, say, 8 and N were 4, one possible microstate of the system would look like this:

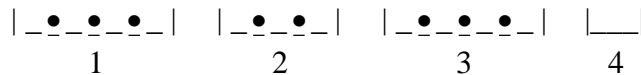


This is a microstate in which oscillator 1 has 1 unit of energy, oscillator 2 has 3, oscillator 3 has none and oscillator 4 has 4.

By reducing *adjacent* vertical lines in this drawing to single lines, and eliminating *all* other lines, a slightly simpler pictorial representation of the above microstate can be constructed. It looks like this:



Another possible microstate of this same macrostate ($U = 8$, $N = 4$) might be



which in simplified notation would correspond to



Thus, for this case, any microstate can be formed by permuting 8 dots and 3 lines in all possible ways. How many such ways are there? Well, there are $8 + 3 = 11$ symbols in all. These symbols have to be laid out one after another in sequence. The first spot in the sequence can be chosen in 11 ways, the second in 10, the third in 9, and so on, till just one spot and one symbol remain. The total number of arrangements one can get from this procedure is therefore

$$11 \times 10 \times 9 \times \cdots \times 3 \times 2 \times 1 \quad (5)$$

But these arrangements would count as distinct those in which the 8 dots were shuffled around amongst each other and the 3 lines were shuffled around amongst each other. So the expression in (5) is an overcount, and to correct it, we divide it both by the number of permutations of the dots, and by the number of permutations of the lines. This gives us

$$\Omega(U=8, N=4) = \frac{11!}{8! \times 3!} = \binom{11}{8} = \binom{11}{3} \quad (6)$$

That is, the number of microstates is the number of combinations of 11 symbols taken 8 at a time, or the number of combinations of 11 symbols taken 3 at a time.

The generalization of this result to any U and any N should now be apparent. It is

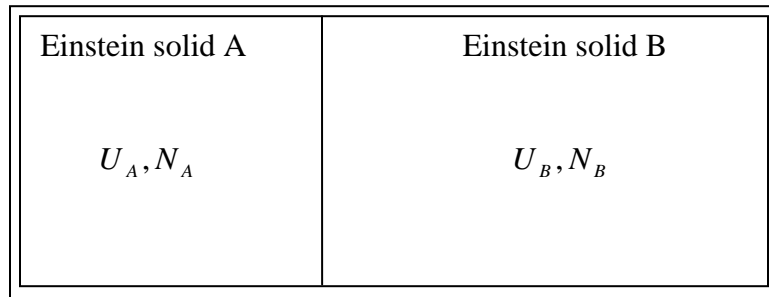
$$\Omega(U, N) = \binom{U+N-1}{U} = \binom{U+N-1}{N-1} \quad (7a)$$

$$= \frac{(U+N-1)!}{U! \times (N-1)!} \quad (7b)$$

It's easily verified that this formula reproduces the results shown in Table 1 for $N=3$ and $U=0, 1, 2$ and 3 .

• Interacting Einstein solids

We can adapt this model to the study of macroscopic systems that aren't isolated from their surroundings but interact with them. Consider, therefore a closed composite system made up of two Einstein solids as shown below.



A can be regarded as the system, and B the surroundings, the two being separated by an internal constraint. (A and B as a whole are isolated from the larger environment surrounding them, and continue to remain isolated from it when other things are done to them.) This internal constraint is no longer an imaginary dividing line, but a physical

boundary, and we'll assume that, initially, the boundary is made of the same material as the outer boundary. This means that initially A and B are completely isolated from each other (and also, of course, from the external surroundings.) But we'll also assume that this material can be changed at any point of time to allow A and B to interact.

There are several ways this interaction can take place. If the internal constraint is made freely moveable, for instance, the collisions of A or B atoms with its surface could potentially move it to one or other side. From mechanics, we know that when objects move – or more technically, when a force is displaced – something called *work* is performed. More generally, in thermodynamics we regard work as a form of energy *transfer* that is completely convertible into the lifting of a weight in the surroundings. We'll have more to say about this later.

Even if the internal constraint were not moveable, energy could still be transferred from A to B or B to A if its material properties were suitably altered. (We won't worry about the nature of this alteration for the moment.) This could happen in the following way: The atoms of A collide with each other and with the atoms in the internal constraint, exchanging energy in the process. The atoms of the internal constraint then interact among themselves and with the atoms of B , likewise exchanging energy in the process. This then leads, in effect, to a transfer of energy from A to B (or vice versa), notwithstanding the fact that the internal constraint remains in exactly the same place. If energy is transferred in this way, we call it *heat*. An internal constraint that permits such an exchange is called *diathermal*, and one that prevents it is called *adiabatic*. These are terms that you now need to understand in this technical sense. We'll have more to say about heat later on too.